# SOME LIMITATIONS AND ERRORS INHERENT IN THE USE OF THE DEW CELL FOR MEASUREMENT OF ATMOSPHERIC DEW POINTS

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#### ABSTRACT

The physics of the dew cell sensor are investigated and the resulting limitations upon application and errors in use are discussed. Specific consideration is given to the measurable range of dew point temperatures and relative humidities, response at different temperatures and under different aspiration conditions, and to errors arising from change in the water of hydration of lithium chloride and from existing absolute humidity gradients. It is concluded that two major sources of difficulty exist with the dew cell: the choice of lithium chloride and the means of aspiration.

## 1. INTRODUCTION

With the advent of requirements to measure atmospheric humidity remotely and automatically, the dew cell has replaced the sling psychrometer in many locations. A few discussions of the operating characteristics and their effects upon climatological records have been presented [2,6]. By considering the operating principle of the sensor alone, most of the significant limitations upon the dew cell and errors encountered in its use can be accounted for. Accordingly, no discussion of the telemetry or readout circuitry is included here.

It is also well to note that another instrument operating upon a similar principle to that of the dew cell is commercially available from Australia [3,9]. This instrument is much more sophisticated, accurate, and correspondingly dear. The differences between these two instruments vividly illustrate the care that inheres in the accurate measurement of humidity.

# 2. OPERATING PRINCIPLE

The operation of the dew cell depends upon the fact that an ionic salt begins to absorb and dissolve in water from the atmosphere as soon as the water vapor pressure of that atmosphere exceeds the water vapor pressure of a saturated solution of that salt. Subsequent decrease of ambient vapor pressure below that of the saturated solution will result in water vapor being given off. Evidently a state of dynamic equilibrium will exist when the two vapor pressures are equal. This may be visualized in figure 1, which provides the quantitative basis for discussing the operation of the dew cell. Consider an atmospheric vapor pressure of A mm. Hg, corresponding to a dew point temperature  $T_d$  in figure 1. Then lithium chloride (LiCl) is in equilibrium with the atmospheric water vapor pressure at the same pressure but higher

temperature  $T_e$ . At precisely this temperature, no net exchange of water takes place. Hence it may be referred to as the equilibrium temperature. It is easily seen that by imposing the requirement that the LiCl be maintained

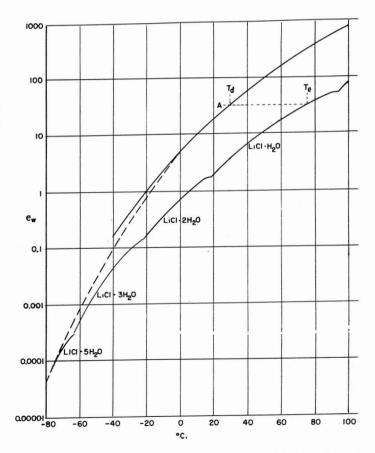


Figure 1.—Vapor pressure of saturated lithium chloride solutions vs. temperature [5, 8].

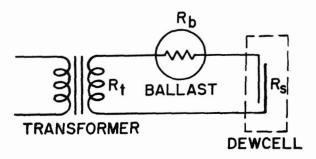


FIGURE 2.—Dew cell electric schematic.

at the equilibrium temperature requires that this temperature follow the changes in atmospheric dew point temperature and be a measure of it.

The means of requiring the lithium chloride to follow changes in atmospheric vapor pressure is straightforward and is shown schematically in figure 2. The salt absorbs water, partially going into solution. Since solutions of LiCl are electrically conductive, current passes through the circuit; but the solution exhibits resistance and joule heating occurs, raising the temperature and tending to drive off water. An equilibrium current is established wherein just sufficient heat is generated to maintain the LiCl at the equilibrium temperature.

## 3. LIMITATIONS OF OPERATION

The operating principle imposes limitations upon the usefulness of the dew cell. Figure 1 immediately provides one limitation. The lowest measurable dew point (frost point) is  $-76^{\circ}$  C., the cryohydric temperature at which LiCl solutions freeze and cease to conduct current.

A limitation exists at the high temperature end of the scale, also, but is not shown and is of no practical interest since the highest dew points encountered in nature may be accommodated by the dew cell.

The range of relative humidities which can be measured by the dew cell may be derived from figure 1. For example, consider an ambient temperature of 30° C. and a relative humidity of 10 percent. The corresponding equilibrium temperature is 27° C., but this is less than the ambient and the dew cell has no provisions for cooling; i.e., it cannot measure 10 percent relative humidity at 30° C. The lowest relative humidity it can measure at this temperature is seen to be the ratio of vapor pressure of a saturated solution of LiCl to that of pure water at the same temperature, or

$$\frac{3.76}{31.8} \times 100 = 11.8$$
 percent relative humidity

Deriving the same quantities for temperatures of interest leads to figure 3, the lowest operating relative humidity at any given ambient temperature. In practice, these may be unattainable because of a severe response problem

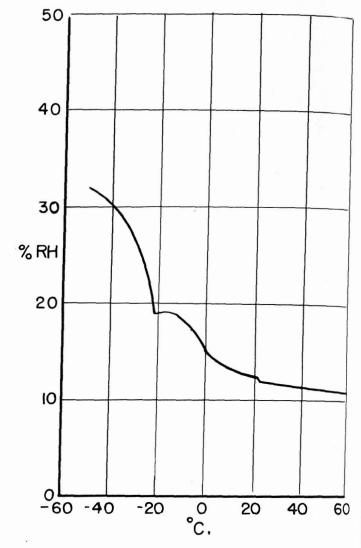


Figure 3.—Lower limitations of operation of dew cell in terms of relative humidity from  $-60^{\circ}$  C. to  $+60^{\circ}$  C.

arising when the equilibrium temperature equals the ambient temperature. A discussion of this follows.

Since the dew cell equates the water vapor pressure of a saturated lithium chloride solution with that of the atmosphere, any change in atmospheric vapor pressure effects a change in equilibrium temperature. This change in the atmospheric vapor pressure must be communicated to the lithium chloride surface; such communication is not instantaneous. Accordingly, the dew cell responds in time to the atmospheric change. By considering the mechanisms of communication between the dew cell and ambient vapor pressure some insight into dew cell response can be gained.

Two mechanisms exist to communicate the ambient vapor pressure change to the dew cell: convection and diffusion. Corresponding to these, dew cell response will be considered as a function of two parameters: (1) The difference between equilibrium and ambient temperatures. (2) The equilibrium temperature.

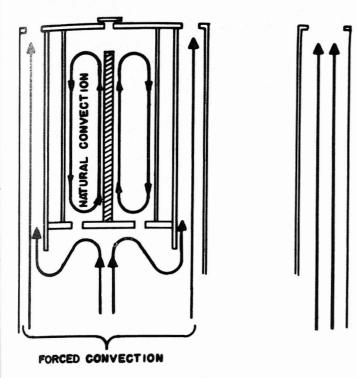


FIGURE 4.—Dew cell enclosure schematic.

In figure 4, the flow of air in the hygrothermometer enclosure is shown schematically. Although forced convection provides some circulation, the air coming into immediate contact with the dew cell circulates by natural convection, or by "the chimney effect." The rate at which this natural circulation occurs is a function of the difference between equilibrium and ambient temperatures,  $T_e - T_a$ . If  $T_e >> T_a$ , then the interior circulation is rapid and any change of atmospheric dew point introduced at the small ports quickly communicates to the dew cell. Conversely, if  $T_{\epsilon} = T_{a}$ , no natural convection occurs and any change in atmospheric dew point communicates slowly by diffusion or by any small disturbance caused by the forced air flow striking the small ports. In addition to the situation depicted in figure 4, the small vent at the top of the dew cell housing is commonly opened to permit some forced ventilation. When  $T_e = T_a$  under these circumstances, some circulation still occurs, but at a considerably diminished rate. In either case, a large value of  $T_e$ — $T_a$  enhances dew cell response.

The second parameter affecting dew cell response, the equilibrium temperature itself, cannot be so summarily treated. It can be demonstrated (see addendum) that the response of the dew cell to a small, step-function change in atmospheric dew point is described by the following equation:

$$\frac{\Delta T}{\Delta T_0} = \exp(-bt), \quad b = \delta \pm \sqrt{\delta^2 - \gamma \tau}$$
 (1)

where  $\Delta T_0$  is the difference in initial and final equilibrium

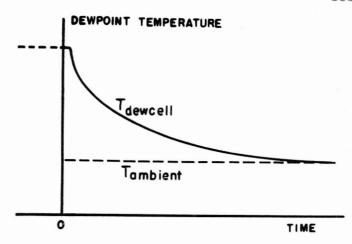


Figure 5.—The nature of dew cell response to small changes in ambient dew point temperature.

temperatures corresponding to the change in atmospheric dew point and  $\Delta T$  is the difference between the final equilibrium temperature and the dew cell temperature (nonequilibrium) at any time. The significance of the other coefficients will be discussed below.

Equation (1) is of the form describing the motion of a viscous damped harmonic oscillator. Three distinct solutions exist depending upon the quantity under the radical sign in b being positive, zero, or negative [7]. To determine which solution applies to the dew cell, a laboratory mockup was subjected to a small step-function change of ambient dew point and a trace of subsequent response obtained similar to that shown in figure 5. In analogy to the harmonic oscillator, the dew cell is strongly "overdamped," or  $\delta^2 >> \gamma \tau$ .

The complete solution for this case is then:

$$\frac{\Delta T}{\Delta T_0} = \frac{b_+}{b_+ - b_-} \exp(-b_- t) - \frac{b_-}{b_+ - b_-} \exp(-b_+ T) \quad (2)$$

where  $b_+$  is associated with the positive sign before the radical and  $b_-$  with the negative. Furthermore, since  $\delta^2 >> \gamma \tau$ ,  $b_+ >> b_-$  and exp  $(-b_+ t)$  may be neglected in equation (2) at time t appreciably greater than zero.

$$\frac{\Delta T}{\Delta T_0} \simeq \frac{b_+}{b_+ - b_-} \exp(-b_- t) \simeq$$

$$\frac{\delta + \sqrt{\delta^2 - \gamma \tau}}{2\sqrt{\delta^2 - \gamma \tau}} \exp\{(-\delta + \sqrt{\delta^2 - \gamma \tau})t\} \quad (3)$$

Immediate interest lies with the response as a function of equilibrium temperature. The measure of response is most conveniently defined as the time required for the dew cell to complete 1/e or 63 percent of the total change. Setting  $\Delta T/\Delta T_0 = 1/e$  and solving equation (3) for t

$$t = \frac{\delta \left(1 + \sqrt{1 - (\gamma \tau / \delta^2)}\right)}{\gamma \tau} \ln \left(\frac{e}{2} \frac{1 + \sqrt{1 - (\gamma \tau / \delta^2)}}{\sqrt{1 - (\gamma \tau / \delta^2)}}\right) \tag{4}$$

Again, since  $\delta^2 >> \gamma \tau$ 

$$t \simeq \frac{\text{constant}}{\gamma_T}$$
 (5)

All terms with significant temperature dependence have already been grouped in  $\tau$ . From the addendum:

$$\tau = \frac{k_2 e_f K_{sp}}{1 - s} \tag{6}$$

where

$$k_2 = \frac{(\text{constant}) (\text{diffusion coefficient})}{(\text{temperature})}$$

 $e_f$ =final equilibrium vapor pressure

 $K_{sp}$ =specific conductivity of saturated LiCl solution

s=solubility of LiCl in water expressed as grams LiCl per gram solution

These quantities may be approximated by:

$$k_2 = (\text{constant}) T_e^{0.75}$$
 (7)

$$e_f = (\text{constant}) \exp(0.0136 T_e)$$
 (8)

$$K_{sp} = (\text{constant}) \exp (0.0197 T_c)$$
 (9)

$$s = 1.64 \times 10^{-3} T_e - 0.045 \tag{10}$$

Then  $\tau$  may be represented by

$$\tau = (\text{constant}) \frac{T_e^{0.75} \exp(0.0333 T_e)}{1.045 - 0.00164 T_e}$$
 (11)

Since t in equation (5) is the time required for the dew cell to complete 63 percent of the change in ambient dew point, the response time at various temperatures may be compared to one taken as  $t_{60}=1$  at  $T_e=60^{\circ}$  C.

$$\frac{t_e}{t_{60}} = \frac{\tau_{80}}{\tau_e} \tag{12}$$

Values of  $t_e/t_{60}$  for various equilibrium temperatures are shown in table 1.

Equation (5) also gives further qualitative support to the effect of the difference between equilibrium and ambient temperatures discussed above. Noting from the addendum that

$$\gamma = \gamma'/h$$
 (13)

equation (5) may be rewritten

$$t \simeq \frac{\mathrm{constant}}{\gamma' \tau} h$$
 (14)

Evidently, decreasing h decreases the time constant. h is a sort of diffusion path length which may be diminished by increasing the rate of natural convection; but its significance does not end there. A different dew cell enclosure design, perhaps with constant forced ventilation, would make the dew cell response reasonably independent of  $T_e - T_a$ . This argument must be taken with caution, however. In the derivation of equation (5) or (14).

Table 1.—Calculated response time constants of the dew cell at various temperatures 1

Equilibrium temperature $T_s$ °C.	Equivalent dew point		t e/t 60
	°C.	°F.	
60	19	66 46	1.0
30	$-3 \\ -13$	27	3. 2
0	$-24 \\ -34$	$-10 \\ -30$	10 18

 $^1$  Data from the laboratory mockup indicated that the time constant of a dew cell is about 1 minute when  $T_e\!\approx\!60^\circ$  C., circulation is by natural convection alone, and  $T_e$  is about 15° C. higher than ambient temperature (25–30 percent relative humidity).

 $\delta^2 >> \gamma' \tau/h$  was assumed. Obviously, decreasing h indefinitely would invalidate the requirement of strong overdamping. Also, attention to the addendum will show that increasing the aspiration to decrease h will simultaneously increase the rate at which heat is dissipated, perhaps even to the extent that heat losses exceed the capability of the dew cell to generate heat. Of course, this is an untenable situation, as Tanner and Suomi [11] demonstrated.

To conclude this discussion of dew cell response, the analysis leading to equation (1) and subsequent equations is subject to two restrictions: (1) That the dew cell be strongly "overdamped." (2) That the change in ambient dew point be small.

The first condition has experimental verification. The second has connection with reality in situations where the ambient dew point temperature is fluctuating rapidly with respect to the rate at which the dew cell can respond.

# 4. ERRORS

Figure 1 provides the basis for discussing an important source of error in the dew cell. At -65.6° C., -20.5° C. +19.0° C., and 94.0° C. lithium chloride in equilibrium with its saturated solution undergoes a phase change, losing water of hydration with increasing temperature. Unfortunately, the available data for LiCl is neither accurate nor complete enough to examine the vapor pressure in the regions near these phase changes in detail. As a possible analogue, calcium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>) is better documented in these regions of phase change. One such region is shown in figure 6. If the atmospheric vapor pressure is between 18.2 and 19.75 mm. Hg., three equilibrium temperatures exist. Which one the dew cell actually would choose if calcium nitrate replaced lithium chloride would be governed by whether the equilibrium temperature was rising, falling, or fluctuating about 42.9° C. Furthermore, the dashed lines in figure 6 represent metastable states which certainly are attainable. If the equilibrium temperature is falling and approaching 42.9° C., two possible future paths exist: either persistence into the metastable region of the Ca(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O curve, or picking up the equilibrium curve Ca(NO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O.

The net effect of passing through these solid phase changes is to introduce a large degree of ambiguity into

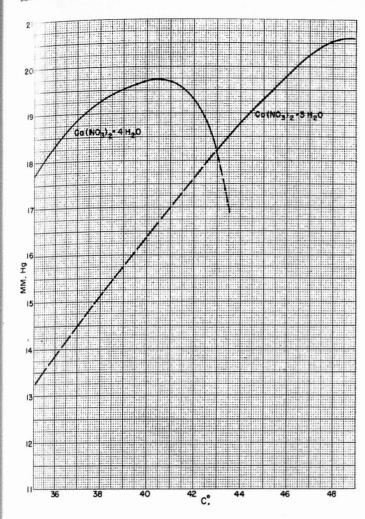


Figure 6.—Vapor pressure of calcium nitrate vs. temperature  $36^{\circ}$  to  $48^{\circ}$  C. [4].

the equilibrium temperature and thus into the dew point. The amount of this ambiguity could be defined with the existence of accurate and complete vapor pressure data for lithium chloride. These data do not presently exist. The solution to this dilemma has been to calibrate the dew cell vs. the sling psychrometer and assume the calibration to hold true under all conditions. Immediately evident is the fact that the dew cell cannot be more accurate than the means of calibration.

Fortunately, there is a simple indication of this error. The loss of a molecule of water of hydration is associated with the evolution of heat from two sources: the thermodynamic latent heat and the abrupt dilution of the LiCl solution requiring the dew cell to react to drive this water off and reestablish equilibrium. Similarly, a gain in water of hydration is accompanied by the absorption of heat. One may anticipate a transient change in temperature upon passage through a region of solid phase change. This would occur at dew points of +40 °C. (+104 °F.), -12 °C. (+11 °F.), -39 °C. (-38 °F.), and -69 °C. (-92 °F.). The magnitude of the transient temperature depends upon the particular phase

change in question, how long the equilibrium temperature remains above or below the temperature of that phase change, and how rapidly the equilibrium temperature changes. Conover [2] mentions a marked heat surge associated with the phase change occurring at the  $+11\,^{\circ}F$ . dew point.

As noted earlier, the dew cell is a device continuously and automatically equating two water vapor pressures. Any discrepancy in this equating process will result in an error in the measured equilibrium temperature, and a similar error in the dew point. The magnitude of this error is given by the Clausius-Clapeyron equation:

$$\frac{\Delta e}{e} = \frac{L}{R_w T_e^2} \Delta T_e \tag{15}$$

or

$$\Delta T_e = \frac{R_w}{L} T_e^2 \Delta \ln e$$

A difference between dew cell equilibrium vapor pressure and that of the atmosphere can arise from two sources. One is the slow response to a change in atmospheric humidity. The second is treated below.

As noted in the addendum, Chapman and Cowling [1] arrived at a most general expression for diffusion in a two-component system. Their equation contains terms treating diffusion as arising from four sources; nonuniformity of composition, pressure, temperature, and external forces. In the dew cell, only composition and temperature gradients are of consequence. Accordingly, the diffusion equation at equilibrium may be written as:

$$\frac{1}{p}\frac{\partial e}{\partial r} - k_T \frac{1}{T} \frac{\partial T}{\partial r} = 0 \tag{16}$$

where

p = total pressure e = water vapor pressure r = radial distance from dew cell  $k_T = \text{thermal-diffusion ratio}$ T = temperature

In words, a temperature gradient leads to a vapor pressure gradient. In the dew cell, if  $T_e > T_a$ , the equilibrium water vapor pressure at the LiCl surface differs from that of the ambient and is greater. Thus, an incorrectly high dew point is recorded. To estimate the magnitude of this effect, equation (16) may be rewritten by considering p=constant

$$\frac{d(e/p)}{d\ln T} = k_T \tag{17}$$

Integrating between the limits of  $e_e$  and  $e_a$  and  $T_e$  and  $T_a$ 

$$\frac{e_e - e_a}{p} = k_T \ln(T_e/T_a) \tag{18}$$

Table 2.—Contribution of absolute humidity gradient to dew cell error

Ambient temperature $T_a$ (°C.)	Relative humidity (percent)	ΔT. (°C.)
-20	20 50	0. 015 0. 23
0	80 20 50	0. 32 0. 08 0. 42
+20	80 20 50	0. 59 0. 17 0. 54
	80	0. 80

Yoshitake [10] has suggested:

$$k_T = 0.32 \frac{e_a}{p} \tag{19}$$

Then, equation (18) becomes

$$\frac{e_e - e_a}{e_a} = \frac{\Delta e}{e_a} = 0.32 \ln (T_e/T_a)$$
 (20)

If

$$\frac{T_e - T_a}{T_a} << 1$$

$$\Delta \ln e \simeq 0.32 \frac{T_e - T_a}{T_a} \tag{21}$$

Substituting this value of  $\Delta$  ln e into equation (15),

$$\Delta T_e = 0.32 \, \frac{R_w}{L} \, T_e^2 \, \frac{T_e - T_a}{T_a} \tag{22}$$

Numerical values may be obtained easily and are shown in table 2.

Two aspects of the aspiration of the dew cell have already been discussed: its relation to response time and the fact that an upper limit on aspiration rate is imposed by the fact that the heat dissipation must not exceed the capacity of the dew cell to generate heat and maintain the equilibrium temperature. In addition to these, aspiration is related to a third effect most significant to the meteorologist, that of "overshoot" or dew point readings exceeding the ambient temperature. This occurs when dew point measurements are made in a fog or mist, because suspended droplets of water are drawn into the hygrothermometer enclosure by the fan (not shown in fig. 4) and some find their way into the higher-thanambient temperature domain surrounding the dew cell element, evaporate, and create a vapor pressure higher than ambient. Of course, the dew cell equates vapor pressures as always, but now indicating an incorrectly high dew point.

The aspiration problems demand conflicting solutions. To minimize response time the aspiration rate must be increased and most desirably by forced convection, but the aspiration rate must be restricted so as not to dissipate

excessive heat. Forced convection must be entirely eliminated if the dew cell is to be free of "overshoot." A possible compromise might be opening the small vent at the top of the dew cell housing in dry climates and closing it in moist climates.

#### 5. CONCLUSIONS

The dew cell offers the principal advantage of being a potentially absolute means of measuring atmospheric dew point with a minimum of instrument. As opposed to the cooled mirror dew point hygrometer, equilibrium detection by resistance rather than photocell output and heating rather than cooling are considerable simplifications.

The existing dew cell has two major sources of difficulties; the choice of lithium chloride and the means of aspiration. Investigations are currently being conducted at the Instrumental Engineering Division to find a suitable replacement for lithium chloride. The difficulties of aspiration might find some alleviation in maintaining the small vent at the top of the dew cell enclosure fully closed in humid climates and partially or fully opened in dry climates. However, the complete solution (if it exists!) will demand more extensive modification than that suggested.

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# **ADDENDUM**

## DERIVATION OF EQUATION (1)

The dew cell responds to a change in atmospheric dew point by absorbing or desorbing water. This, in turn, causes a change in equilibrium temperature in the appropriate direction until equilibrium is reestablished. Considering this process in detail:

$$dQ = CdT$$
 (1A)

where Q=heat energy, C=dew cell heat capacity, T=temperature of dew cell.

$$dQ = dQ_{tn} - dQ_{out} \tag{2A}$$

Referring to figure 2

$$\frac{dQ_{\rm in}}{dt} = I^2 R_s = I^2 / K_s \tag{3A}$$

where  $K_s$ =conductance of the lithium chloride layer and

$$I = \frac{E_i}{R_t + R_b + R_s} \simeq \frac{E_i}{R_s} = E_i K_s, \quad R_s > > R_t + R_b \quad (4A)$$

where  $E_i$ =transformer secondary voltage.

$$K_s = K_{sp} \frac{a}{I} \tag{5A}$$

where

 $K_{sp}$ =specific conductivity of LiCl solutions a=cross-sectional area of LiCl between electrodes l=electrode spacing

$$al = \frac{m + m_L}{d_s} \tag{6A}$$

where m=mass of water in solution,  $m_L=$ mass of LiCl in solution, and  $d_s=$ density of solution

$$al = \frac{m}{d_s(1-s)} \tag{7A}$$

where s=solubility of LiCl in water expressed as grams LiCl per gram solution. Substituting equation (7A) into (5A)

$$K_s = K_{sp} \frac{m}{d_s l^2 (1 - s)} \tag{8A}$$

Thus:

$$\frac{dQ_{\text{in}}}{dt} = \frac{E_i^2 K_{sp} m}{d_s l^2 (1-s)} \tag{9A}$$

$$\frac{dQ_{\text{out}}}{dt} = k_1(T - T_a) \tag{10A}$$

Substituting equations (9A) and (10A) into (1A)

$$\begin{split} \frac{dQ}{dt} &= \frac{dQ_{\text{ln}}}{dt} - \frac{dQ_{\text{out}}}{dt} = \frac{E_{i}^{2}K_{sp}m}{d_{s}l^{2}(1-s)} - k_{1}(T-T_{a}) \\ &= C\frac{dT}{dt} \end{split} \tag{11A}$$

Solving for m and differentiating:

$$\frac{dm}{dt} = \frac{Cd_s l^2 (1-s)}{E_t^2 K_{sp}} \frac{d^2 T}{dt^2} + \frac{k_1 d_s l^2 (1-s)}{E_t^2 K_{sp}} \frac{dT}{dt}$$
 (12A)

The rate at which water vapor is brought to the LiCl surface is governed by a general diffusion equation [1]. Unfortunately, the expression for dm/dt obtained from such an equation yields a complicated and cumbersome (if soluble) differential equation when substituted into equation (12A). In place of it, it may reasonably be assumed that the rate of mass transport of water vapor to the dew cell is proportional to the vapor pressure gradient between the LiCl surface and the ambient.

$$\frac{dm}{dt} = K_2 \frac{S}{h} \left( e_a - e \right) \tag{13A}$$

where

S=exposed area of LiCl surface

h=distance between the LiCl surface and ambient\*

 $k_2$  = constant of proportionality\*\*

 $e_a$  = ambient water vapor pressure

e=water vapor pressure at temperature T

Although the Clausius-Clapeyron equation would most rationally approximate the vapor pressure of saturated LiCl solution, its use, like that of the exact diffusion equation, leads to a difficult second-order, nonlinear differential equation. From figure 1, it is not unreasonable to represent the water vapor pressure of LiCl in the range  $-30\,^{\circ}$  C. to  $+60\,^{\circ}$  C. by:

$$e = \exp(\alpha T + \beta)$$
 (14A)

Substituting equation (14A) into (13A) and collecting terms:

<sup>\*</sup>h is a very ill-defined quantity, since it is closely related to the interior natural convection treated in the text. For the purposes of this discussion it suffices to regard it as an equivalent diffusion path length without geometric reference to the dew cell enclosure.

<sup>\*\*</sup>Rigorously,  $k_2$  is not a constant, containing the term D/T where D is the diffusion coefficient and T a temperature between the limits  $T_\epsilon$  and  $T_a$ . But, as will be seen, the derivation treats only the case for small changes in  $T_\epsilon$ . Under these circumstances,  $k_2$  can be regarded as a constant. In fact, this assumption is implicit in the differentiation by t used to obtain equation (12A) where  $K_{\epsilon p}$  and s are functions of temperature, but the variation of their temperature dependences with time is of the second order.

$$\frac{dm}{dt} = k_2 \frac{S}{h} e_f [1 - \exp \left\{ \alpha (T - T_f) \right\}]$$
 (15A)

where  $e_f$ =final equilibrium vapor pressure (equal to  $e_a$ ) and  $T_f$ =final equilibrium temperature. If  $|\alpha(T-T_f)|$  <<1

$$\frac{dm}{dt} = -k_2 \frac{S}{h} e_f \alpha (T - T_f)$$
 (16A)

Combining equations (16A) and (12A)

$$\frac{d^{2}T}{dt^{2}} + \frac{k_{1}}{C} \frac{dT}{dt} + \frac{S\alpha E_{i}^{2} k_{2} e_{f} K_{sp}}{Ch d_{s} l^{2} (1-s)} (T - T_{f}) = 0$$
 (17A)

setting  $\gamma = S\alpha E_i/Cd_s l^2 h$ ,  $\tau = k_2 e_f K_{sp}/(1-s)$ , and  $\Delta T = T - T_f$ 

$$\frac{d^2\Delta T}{dt^2} + \frac{k_1}{C} \frac{d\Delta T}{dt} + \gamma \tau \Delta T = 0 \tag{18A}$$

Applying the boundary conditions that:

at 
$$t=0$$
  $\Delta T = \Delta T_0$   $\frac{d\Delta T}{dt} = 0$ 

the solution is:

$$\frac{\Delta T}{\Delta T_0} = e^{-bt}, \quad b = \frac{k_1}{2C} \pm \sqrt{\left(\frac{k_1}{2C}\right)^2 - \gamma \tau}$$
 (19A)

Equation (19A) is identical with equation (1).